

the same scale as Rowland's maps would not only be valuable in itself, but would be likely to fill in some of the origins in the deplorably long list of unidentified lines in the solar spectrum. The region usually employed in radial velocity determinations might receive first attention.

Note on the Application of Van der Waals' Equation to Solutions.

By the EARL OF BERKELEY.

(Communicated by Professor J. Larmor, Sec. R.S. Received January 11,—Read January 24, 1907.)

In a recent communication to the Royal Society* by Mr. Hartley and myself, the results are given of some measurements of the osmotic pressures of strong aqueous solutions of cane sugar, dextrose, galactose, and mannite.

It may be of interest to inquire how far these results can be represented by an equation on the plan of that introduced by Van der Waals to express the relation between the pressures, volumes, and temperatures of gases and vapours.

The Van der Waals equation is $(P + a/v^2)(v - b) = RT$, and the two that I have found which fit the present case are

$$(A/v - p + a/v^2)(v - b) = RT, \quad (1)$$

$$(A/v + p - a/v^2)(v - b) = RT. \quad (2)$$

The approximation of this form of equation is, perhaps, enhanced when it is taken into consideration that some 50 modifications of Van der Waals' equation were tried. Among these were various possible conceptions which might underlie the meaning of the volume term as applied to solutions, besides modifications of the coefficients a and b , in which these constants were assumed to be some function of either the volume or the pressure. Dieterici's equation of state was also tried with two or three different conceptions of " v ."

In the following application of the equations, the units are atmospheres and litres, and R is the gas constant taken as equal to 0.08207. In equation (1) the v is the volume of solvent which contains 1 gramme molecular weight of solute, and in equation (2) it is the volume of solution which

* 'Phil. Trans.,' A, vol. 206, p. 503.

contains the gramme molecular weight. Both of them are derived from the densities of the solutions at $0^{\circ}\text{C}.$; and the osmotic pressures, together with the absolute temperature T , refer to that temperature.

In the tables, column I gives the concentration in grammes per litre of solution, II gives the v of equation (1), III the v of equation (2), IV and V the calculated osmotic pressures corresponding to II and III respectively, while column VI gives the observed osmotic pressure.

Cane Sugar.

I. Concentration.	II. v of (1).	III. v of (2).	IV. Calculated osmotic pressure.	V. Calculated osmotic pressure.	VI. Observed osmotic pressure.
850	0.18270	0.39722	(183.0)	(183.0)	(183.0)*
760	0.23656	0.45025	(133.7)	(133.7)	(133.7)
660	0.29883	0.51177	(100.8)	(100.8)	(100.8)
540	0.41431	0.62570	68.4	67.7	67.5
420	0.59471	0.80492	45.0	43.4	44.0
300	0.91883	1.12764	27.7	25.4	26.8
180	1.67368	1.88094	14.6	12.2	14.0

The v 's of column II are calculated from Landolt and Bornstein's tables of densities of cane sugar solutions, by finding the change in volume of the solution caused by the addition of 1 gramme of water, and multiplying this by the weight of water which contains 1 gramme molecule of solute. These numbers are given to one significant figure beyond what can here be utilised.

The numbers given in the fourth and fifth columns were calculated, by trial and error, from the equations when applied to the osmotic pressures of the first three concentrations given in the table. The resulting constants were then substituted and the p calculated for the other cases.

The constants for equation (1) are

$$A = 45.3689, \quad a = 3.5696, \quad b = 0.05266,$$

while those for equation (2) are

$$A = 6.7166, \quad a = 7.2960, \quad b = 0.25139.$$

* This value is derived from vapour-pressure measurements. It will be seen, on p. 505 of the communication referred to above, that all the osmotic pressures, obtained from the vapour pressures, are somewhat higher than those measured directly; consequently, the osmotic pressure obtained from the vapour pressure of a solution of 850 grammes in the litre was proportionately reduced so as to bring it into line with those measured directly.

Dextrose.

I. Concentration.	II. v of (1).	III. v of (2).	IV. Calculated osmotic pressure.	V. Calculated osmotic pressure.	VI. Observed osmotic pressure.
549	0·21326	0·32435	(121·2)	(121·2)	(121·2)
449	0·28601	0·39664	(87·9)	(87·9)	(87·9)
319	0·44838	0·55824	(53·2)	(53·2)	(53·2)
200	0·78438	0·89357	28·8	28·4	29·2
100	1·67913	1·78789	12·9	12·4	13·2

The material for calculating the v 's of column II in the manner explained for cane sugar was not at hand; as it is known that there is but a small change in volume on dilution, it was considered that the weight of water containing 1 gramme molecule would be close enough for the purpose in view, and it was therefore used. It must be remembered that the dextrose itself was not quite pure,* so that the osmotic pressures are possibly slightly inaccurate.

The calculated osmotic pressures are obtained as in the case of cane sugar and the constants are for equation (1)

$$A = 43\cdot0512, \quad a = 3\cdot0089, \quad b = 0\cdot06069;$$

and for equation (2)—

$$A = 3\cdot3845, \quad a = 2\cdot9706, \quad b = 0\cdot10762.$$

On comparing the agreement between the calculated and observed osmotic pressures, there seems to be but little difference between the two equations. On the whole, equation (1) appears to be the better fit over the present range; though it is probable that the other one, having the positive sign for p , may replace it at high dilutions.

There is apparently another way of testing the ranges of these equations. The system of curves which represent either of them, for different values of T , has features similar to those of the well-known diagram of isothermals for vapour-liquid substances such as carbonic acid. Now, the reasoning originally applied by J. Thomson to Andrews' experiments on gas-pressures admits of extension to the present case. If we draw the system of p, v curves as mentioned above, then when the temperature is high, p will diminish throughout the curve as v increases; on passing in succession to curves corresponding to lower temperatures, one will be reached for which the

* *Loc. cit.*, p. 497.

gradient or slope just vanishes at a certain pressure ; and the curves beyond this will have contrary flexure in different parts.

Now, increase of osmotic pressure with increase of dilution must involve intrinsic physical instability, resulting in change of state ; and the characteristic equation, together with the derived equations $dp/dv = 0$ and $dp^2/dv^2 = 0$, will determine the critical temperature (and the pressure and volume) below which supersaturation and crystallisation can set in.

The values of T , p , v , for the critical point derived in this way from equations (1) and (2) for cane sugar are impossible ones, being respectively

$$T = 583^{\circ}4, \quad p = -2\cdot01, \quad v = 0\cdot477,$$

$$\text{and} \quad T = -72^{\circ}44 \quad p = 7\cdot98, \quad v = 0\cdot612.$$

As crystallisation can take place at ordinary temperatures, the p, v curve must show a double bend somewhere near the point at which this occurs ; equation (1) shows part of such a bend,* but not equation (2).

We might, therefore, find the point on the curve for $T = 273^{\circ}$, at which $dp/dv = 0$, where complete instability sets in for that temperature ; but even if the equation held good up to this point, it would merely be the point of maximum possible supersaturation at that temperature, and would not be easily amenable to experiment. Graphs of equation (1) give this upper limit of supersaturation as being at the following values of v :—for cane sugar, $v = 0\cdot092$, for dextrose, $v = 0\cdot12$.

Although equation (2) cannot hold up to the point of saturation, yet, for moderate dilutions, this equation can be inferred from certain theoretical considerations (see *infra*), provided b is the difference between the v 's in columns II and III of the tables ; this is seen to be the case for dextrose, and not very far different for cane sugar.† The relation ought theoretically to come out better when the value of b is determined from the lower pressures instead of the higher ; the constants A and a , as given above, from the higher observations, seem too big compared with the main term RT .

The point of maximum supersaturation may be estimated in a qualitative way by means of the results obtained with galactose and mannite. The test will probably be still more imperfect, because in the case of galactose that substance was impure,‡ and in the case of mannite the experiments themselves were not very good,§ and also because the observed osmotic

* These graphs are somewhat similar to that of Van der Waals' equation as applied to carbon dioxide at -20° C.

† It is interesting to note that this value of b for cane sugar in the equation $p(v-b) = RT$ satisfies the lowest observation exactly.

‡ *Loc. cit.*, p. 501.

§ *Loc. cit.*, p. 501.

pressures are too close together to define the constants with sufficient accuracy.

Galactose.

Mannite.

I. Concentration.	II. v of (1).	III. Observed osmotic pressure.	I. Concentration.	II. v of (1).	III. Observed osmotic pressure.
500	0·24587	95·8	125	1·3281	16·7
380	0·35660	62·8	110	1·5251	14·6
250	0·60394	35·5	100	1·6897	13·1

The v 's under column II are, in both cases, the weight of water containing 1 gramme molecule of the solute.

The constants for equation (1) when applied to galactose are

$$A = 41\cdot90, \quad a = 2\cdot377, \quad b = 0\cdot0492;$$

and, from the graph, $dp/dv = 0$ at about $v = 0\cdot095$.

The constants for mannite are

$$A = 38\cdot89, \quad a = 25\cdot19, \quad b = 0\cdot494;$$

and $dp/dv = 0$ at about $v = 0\cdot98$.

Thus, finally, notwithstanding the tempting analogy with Van der Waals' equation, shown by the graphs for equation (1) and by the values of b in equation (2), it has appeared that it is only possible to regard these equations, pending further experimental work, as holding good over a limited range of values.

There is one further theoretical consideration which may be touched upon. It is evident that if one could find a membrane which is only permeable to the *solute*, then when the solution is placed in contact with the pure liquid solute through this membrane, an osmotic pressure will be set up. The p, v curves representing these new osmotic pressures and volumes will show phenomena, in connection with the freezing point of the solution, analogous to those discussed above as appertaining to the crystallising point. In other words, the freezing and crystallising points of a solution are two extreme points, with continuous physical transition between them representable by the equations of osmotic pressure.

[February 1.—In connection with the preceding paragraph, Professor Iarmor has suggested the following generalisation :—

If P is the osmotic pressure, p' the vapour pressure, and T the temperature, then for all aqueous solutions*

$$P = \text{same function of } p' \text{ and } T. \quad (i)$$

Moreover, the freezing point is the temperature for which p' , for the solution, is the same as for ice (thus, incidentally, isotonic solutions have the same vapour pressures and the same freezing point). Now, for ice,

$$p' = \text{function of } T. \quad (ii)$$

Equation (i) represents the surface characteristic of water as a solvent; the equation (ii) represents a cylinder parallel to the axis of P . These two surfaces intersect along a curve, which is the freezing curve characteristic of all solutions in water. At each freezing point both P and p' are definite functions of that temperature, the same for all solutions. Thus, to go to a particular case, so far as the equation $P = RT/(v-b)$ holds good—or rather more generally, so far as osmotic pressure depends only on the temperature and on the volume of the water present (with 1 gramme molecule of solute)—then to that extent the freezing point of any aqueous solution depends only on this same volume; *i.e.*, to that extent the freezing point depends only on the concentration of the solution, when estimated on the water present, instead of on the volume of solution. At high dilution it may be taken as simply proportional to this concentration.]

The theoretical considerations that favour the relation (2) for moderate concentrations are, as expressed by Professor Larmor, briefly as follows:—The available (or free) energy of a solution at any given constant temperature can depend only on the ratio of the masses of solute and solvent present; it is, therefore, a function of the ratio of the mass of the solute (a gramme equivalent) to the volume of water present; the latter is $v-b$ where v is the volume of the solution and b may be taken as constant. The general reasoning of Willard Gibbs,† applicable to any very dilute system, shows that this function must be of the form $-C \log(v-b)$. Now the variation of this available energy must be equal to $-pdv$; hence, $p = C/(v-b)$. At extreme dilution b is negligible compared with v , and the usual argument shows that $C = RT$.

* In 'Roy. Soc. Proc.,' Series A, vol. 77, pp. 156—169, Mr. Hartley and I have established the following relation between the osmotic and vapour pressures of a solution— $P = \frac{As}{\sigma} \log_e \frac{p}{p'}$. Owing to some mistake, it was omitted, in that communication, to point out that for a given temperature, as A , s , σ , and p are constants for any one solvent, all solutions which have the same vapour pressures will have the same osmotic pressures.

† J. W. Gibbs, 'Scientific Papers,' vol. 1, p. 137.

This reasoning has assumed that the molecular complexes of the solute are so far apart as not sensibly to influence each other directly. We can extend its range to stronger concentrations by introducing a correction for such mutual influence. The argument used by Van der Waals indicates that mutual attraction between the molecules of the solute affects p by the addition of a term $-a/v^2$, while here we have also mutual attraction between the solute molecules and the solvent which is similarly expressible by a term $-A/v$. Thus in the equation above it is $p + a/v^2 + A/v$ that should occur instead of p , giving finally $(p + a/v^2 + A/v)(v - b) = RT$.

Indeed, without this special explanation we might, perhaps, have asserted at once that the indirect influence of concentration on p must be expressible as a series $-A/v - a/v^2 - e/v^3 - \dots$, virtually as in (2).

It will be of interest to compare the values of b , for which the equation $p(v - b) = RT$ has been found empirically to represent many solutions, by Abegg, Noyes, and others, with the solution-volume of the gramme-equivalent of solute that is concerned; especially as it has been pointed out* that the equation of reaction of Guldberg and Waage can be founded on this latter form of relation as well as on the simple Boyle-Avogadro one.

It will be noticed that the difference between these two types of equation is that the former does not insist on the asymptotic line of the p, v curve passing through the origin, but allows it to pass at a distance b from it measured along the v axis. This freedom is sufficient to account in a general way for the superiority of the first form, when v is still large; but we have here gone beyond general considerations by giving reasons in favour of a special value of b . The question also remains whether, in the new form, RT actually corresponds to the universal gas-constant; it must do so in gas theory, but the application of the doctrine of available energy to osmotics leaves room for slight discrepancy caused by the attraction of the solvent, such as is indicated in the term A/v *supra*. In the experiments of E. H. Griffiths with cane sugar, at extreme dilution the gas-constant is verified within 0.01 per cent.; this would show that within the range of application of the formula, A cannot be more than about this percentage of RT , which is almost negligible.

I am glad to have the opportunity of thanking Professor Larmor for the kindly advice which he has freely bestowed on this and other work connected with osmotics.

* See T. B. Robertson, 'Journ. Phys. Chem.,' vol. 10, pp. 521—528.